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PRODUCTION OF POLYETHYLENE
TEREPHTHALATE

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This invention relates to an improved method for preparing a synthetic linear polyester which is essentially the condensation product of a dihydric alcohol and a dibasic acid, and more particularly to the preparation of polyethylene terephthalate, a fiber-forming synthetic linear polyester.

The production of the novel class of fiber-forming, linear polyesters of terephthalic acid and a glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$ where n is an integer from 2 to 10 inclusive, is fully disclosed in copending Whinfield and Dickson application Serial No. 618,398, filed September 24, 1945 now U. S. Patent 2,465,319. From the commercial standpoint one of the most attractive polymers of this class is polyethylene terephthalate, and the most promising process for its production comprises carrying out an ester interchange between ethylene glycol and dimethyl terephthalate to form bis-2-hydroxy-ethyl terephthalate monomer which is polymerized to polyethylene terephthalate under reduced pressure (below atmospheric pressure) and at elevated temperatures.

However, in the practice of this process it was observed that dimethyl terephthalate and ethylene glycol, when used in the highly purified state (obviously essential to the formation of a uniform high quality product), were very sluggish with respect to ester interchange. It was noted that less finely purified reagents would undergo the interchange, but the reaction was still too slow for commercial use. Also, it was found on analysis that actually the polymer was not pure polyethylene glycol terephthalate but rather a copolymer with diethylene glycol terephthalate the presence of the diethylene glycol residues in the polymer chain being the result of dimerization of ethylene glycol during the polymerization process. There appear to be three factors influencing the extent of the dimerization: time, temperature and catalyst. It seems that high temperatures and, of course, long polymerization cycles (necessary if catalyst is not used) favor the formation of diethylene glycol. The presence of the diethylene glycol residue in the polymer chain changes the properties of the resultant polymer when present in quantities larger than 2%–3%, and results in a yarn having impaired physical and chemical properties. Furthermore, the diethylene glycol component tends to lower the melting point and increase the tendency of the resultant polymer to degrade under stringent conditions of chemical action. Many catalysts have been suggested for speeding up the reac-

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tion at lowered temperatures whereby to inhibit the undesirable formation of diethylene glycol, and to render the process commercially attractive. Suggested catalysts heretofore found useful in ester interchange reactions are sodium, lithium, potassium, calcium, magnesium, zinc, cadmium, and manganese, as well as alkali metals in the form of their carbonates or other alkaline-reacting salts, for example, the borates; also the oxides of various of these metals. These catalysts, however, are not useful over the entire range of molecular weights desired in the final polymer, and while many of them can produce polymeric ethylene terephthalate with an intrinsic viscosity in the vicinity of 0.6–0.7, when a polymeric material is desired having an intrinsic viscosity in the vicinity of 1.0–2.0, these catalytic materials are not satisfactory.

The expression "intrinsic viscosity," denoted by the symbol $(\eta)_0$, is used herein as a measure of the degree of polymerization of the polyester and may be defined as

$$\lim_{C \rightarrow 0} \frac{\ln(\eta_r)}{C} \text{ as } C \text{ approaches } 0$$

wherein η_r is the viscosity of a dilute phenol-tetrachlorethane (60:40) solution of the polyester divided by the viscosity of the phenol-tetrachlorethane mixture per se measured in the same units at the same temperature, and C is the concentration in grams of polyester per 100 cc. of solution.

An object of this invention therefore is to accelerate and desirably control the reaction between ethylene glycol and dimethyl terephthalate and the subsequent polymerization of the resulting reaction product.

Another object is to prepare from ethylene glycol and dimethyl terephthalate, by a simple and economical expedient, fiber-forming polyethylene terephthalates substantially free of copolymers of polyethylene terephthalate with diethylene glycol terephthalate.

Still another object is to satisfactorily catalyze the ester interchange between ethylene glycol and dimethyl terephthalate and the subsequent polymerization whereby to form a fiber-forming linear polyester of high quality. These and other objects will more clearly appear hereinafter.

Unexpectedly I have found that the ester interchange between ethylene glycol and dimethyl terephthalate, and subsequent polymerization of the resulting bis-2-hydroxy-ethyl terephthalate under super polyester-forming conditions is accelerated to a satisfactory degree in the presence of cata-